

STUDY ON THE DECOMPOSITION OF CUMENE AND TETRALIN HYDROPEROXIDES WITH COBALT ACETATE TETRAHYDRATE ACTIVATED BY BROMIUM ADDITIVES

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The decomposition of cumene and tetralin hydroperoxides under action of cobalt acetate tetrahydrate, sodium bromide and N-bromosuccinimide (NBS) present simultaneously and separately in the system has been studied, since the latter are used as catalysts and activators in the liquid phase oxidation of methylaromatic hydrocarbons. Cumene and tetralin hydroperoxides decompose with highest initial rate in presence of $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ and NaBr in the system. On the basis of the kinetic studies a most probable mechanism for the decomposition of cumene hydroperoxide with cobalt acetate tetrahydrate activated by bromium additives is suggested.

In the study on the oxidation of methylaromatic hydrocarbons in presence of cobalt acetate tetrahydrate and sodium bromide, along with the decomposition of the hydroperoxides at the initial stage of the reaction forming free radicals in the system, the possibility of a direct initiation of the reaction *via* an oxygen complex formation between the cobalt acetate bromide complex and the oxygen molecule was also studied¹. The competition between the two possible initiation reactions will depend on the electron-acceptor properties of oxygen and of the corresponding hydroperoxide with respect to the catalyst.

The purpose of the present paper is to study the catalytic decomposition of cumene (CHP) and tetralin (THP) hydroperoxides with $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ and NaBr present simultaneously and separately in the system, since the latter are used as catalysts and activators in the liquid phase oxidation of methylaromatic hydrocarbons²⁻⁶. In our earlier works we have shown that bromides of the elements from group V of the periodic table – PBr_3 , NBS, SbBr_3 may be used as activators upon oxidation of hydrocarbons in presence of $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ (ref⁷⁻⁸). Another purpose of the present paper is to study the behaviour of $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ system activated by NBS as a peroxide decomposing agent.

There are comparatively few reports in the literature on investigations studying the decomposition of hydroperoxides in presence of $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ activated with bromium additives⁹⁻¹². Chervinskii⁹ has not observed decomposition of cumene hydroperoxide at 70°C in presence of NaBr only, but he has established that the decomposition proceeds in presence of both NaBr and neozone-D. Onuma and coworkers¹¹ investigated the effect of halogenated compounds in presence of $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ on the catalytic decomposition of tert-butyl hydroperoxide. The estab-

lished that the $\text{LiBr}/\text{CoAc}_2$ system reduces the rate of decomposition of the tert-butyl hydroperoxide as compared to that of the cobalt acetate. It was assumed further that the increase of the oxidation rate in presence of $\text{CoAc}_2/\text{LiBr}$ is not attributed to an increase of the rate of the degenerate branching of the chains on hydroperoxide decomposition but it is due to another reaction. Sapunov has shown¹² that cobalt monobromide is the most active catalyst on decomposition of the hydroperoxide. The latter has been proved by the fact that the decomposition of the hydroperoxide of ethylbenzene with cobalt dibromide is characterized with presence of induction period.

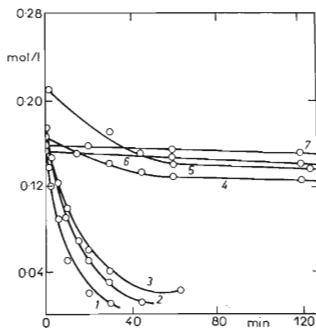
EXPERIMENTAL

Cumene hydroperoxide was purified by methods illustrated in ref.¹³. The hydroperoxide of tetralin was obtained according to methods given in ref.¹⁴. Then it was purified by a threefold recrystallization from light petroleum and has m.p. 55.5°C . The catalysts were purified by recrystallization. The decomposition of the hydroperoxides was studied in a thermostatic glass reactor supplied with a magnetic stirrer and fitted for periodical sampling. The experiments were performed at 80°C in a nitrogen atmosphere. The decompositions were carried out in a glacial acetic acid-pseudocumene solution with a ratio of 1 : 1. The glacial acetic acid was purified using methods¹⁵, whereas pseudocumene was purified by methods illustrated in ref.¹⁶. The consumption of the peroxides was measured by iodometric titration¹⁷. The infrared spectra were taken in a chloroform solution by means of IR-10 apparatus (Zeiss, Jena). The products of cumene hydroperoxide decomposition were analyzed by gas-liquid chromatography on a Perkin-Elmer chromatograph. The conditions and methods used are described in ref.¹⁸.

RESULTS AND DISCUSSION

The kinetic curves for the decomposition of cumene hydroperoxide are shown in Fig. 1, while those for the decomposition of tetralin hydroperoxide are presented in Fig. 2. In Fig. 3 are shown the kinetic curves of decomposition of CHP at various

FIG. 1
Catalytic Decomposition of Cumene Hydroperoxide at 80°C in a Glacial Acetic Acid-Pseudocumene Solution with a Ratio of 1 : 1 in a Nitrogen Atmosphere in the Presence of 1 $[\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}] = 5 \cdot 10^{-3} \text{ mol/l}$ and $[\text{NaBr}] = 1 \cdot 10^{-2} \text{ mol/l}$, 2 $[\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}] = 5 \cdot 10^{-3} \text{ mol/l}$ and $[\text{NBS}] = 1 \cdot 10^{-2} \text{ mol/l}$, 3 $[\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}] = 5 \cdot 10^{-3} \text{ mol/l}$, 4 $[\text{NaBr}] = 1 \cdot 10^{-2} \text{ mol/l}$, 5 Thermal Decomposition, 6 $[\text{NaBr}] = 1 \cdot 10^{-2} \text{ mol/l}$ and $[\text{NBS}] = 1 \cdot 10^{-2} \text{ mol/l}$, 7 $[\text{NBS}] = 1 \cdot 10^{-2} \text{ mol/l}$



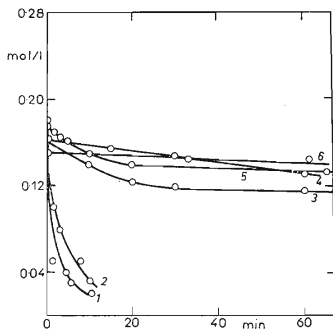


FIG. 2

Catalytic Decomposition of Tetralin Hydroperoxide at 80°C in a Glacial Acetic Acid-Pseudocumene Solution with 1 : 1 Ratio in a Nitrogen Atmosphere in the Presence of 1 [CoAc₂.4 H₂O] = 5 · 10⁻³ mol/l and [NaBr] = 1 · 10⁻² mol/l, 2 [CoAc₂.4 H₂O] = 5 · 10⁻³ mol/l, 3 [NaBr] = 1 · 10⁻² mol/l, 4 [NaBr] = 1 · 10⁻² mol/l and [NBS] = 1 · 10⁻² mol/l, 5 [NBS] = 1 · 10⁻² mol/l, 6 Thermal Decomposition

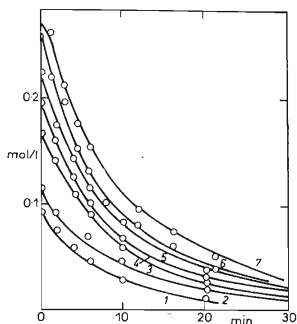


FIG. 3

Catalytic Decomposition of Cumene Hydroperoxide at 80°C in a Glacial Acetic Acid-Pseudocumene Solution with 1 : 1 Ratio in a Nitrogen Atmosphere in the Presence of 5 · 10⁻³ mol/l CoAc₂.4 H₂O and 1 · 10⁻² mol/l NaBr at Various Initial Concentrations of the Hydroperoxide: 1 [CHP] = 0.09 mol/l, 2 [CHP] = 0.12 mol/l, 3 [CHP] = 0.17 mol/l, 4 [CHP] = 0.20 mol/l, 5 [CHP] = 0.23 mol/l, 6 [CHP] = 0.27 mol/l, 7 [CHP] = 0.31 mol/l

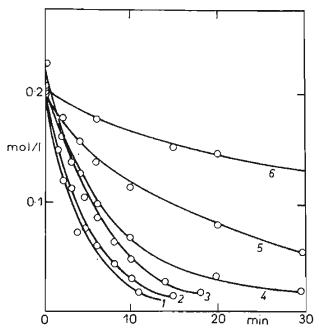


FIG. 4

Catalytic Decomposition of Cumene Hydroperoxide with Initial Concentration of c. 0.2 mol/l at 80°C in a Glacial Acetic Acid-Pseudocumene Solution with Ratio of 1 : 1 in a Nitrogen Atmosphere in the Presence of Various Concentrations of the CoAc₂.4 H₂O Catalyst and NaBr Activator with a Ratio of 1 : 2; 1 [CoAc₂.4 H₂O] = 1 · 10⁻² mol/l and [NaBr] = 2 · 10⁻² mol/l, 2 [CoAc₂.4 H₂O] = 8.5 · 10⁻³ mol/l and [NaBr] = 1.7 · 10⁻² mol/l, 3 [CoAc₂.4 H₂O] = 6.5 · 10⁻³ mol/l and [NaBr] = 1.3 · 10⁻² mol/l, 4 [CoAc₂.4 H₂O] = 5 · 10⁻³ mol/l and [NaBr] = 1 · 10⁻² mol/l, 5 [CoAc₂.4 H₂O] = 2.5 · 10⁻³ mol/l and [NaBr] = 5 · 10⁻³ mol/l, 6 [CoAc₂.4 H₂O] = 1.25 · 10⁻³ mol/l and [NaBr] = 2.5 · 10⁻³ mol/l

initial concentrations of the hydroperoxide and in Fig. 4 are given the curves of decomposition of CHP at various initial concentrations of the catalyst ($\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$) and activator (NaBr) with a constant ratio of 1 : 2.

The treatment of the experimental results from the decomposition of cumene and tetralin hydroperoxides was done by performed using the Minsk-32 computer. The equations for the curves of decomposition were obtained and the initial rates of decomposition of cumene and tetralin hydroperoxides and the respective rate constants were determined (Table I). The parameters given in Table II were obtained in the study of the order with respect to the hydroperoxide and the catalyst concentration on decomposition of cumene hydroperoxide. The initial rate of decomposition of cumene hydroperoxide is highest in presence of $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ and NaBr ($3 \cdot 2 \cdot 10^{-4} \text{ mol/l s}$). The initial rate as compared to a rate of decomposition proceeding

TABLE I
Catalytic Decomposition of Cumene Hydroperoxide (CHP) and Tetralin Hydroperoxide (THP)

Hydroperoxide	Catalyst and activator	$10^5 \cdot w, \text{ mol/l s}$		Equation	$K, \text{ min}^{-1}$	
		exp.			calc.	exp.
CHP	$\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$	14	12	$c = 0.17 \exp(-0.05\tau)$	0.05	0.04
CHP	$\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$	36	32	$c = 0.19 \exp(-0.11\tau)$	0.11	0.11
CHP	$\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ + NaBr	18	18	$c = 0.17 \exp(-0.06\tau)$	0.06	0.06
CHP	NaBr + NBS	4.1	3.2	$c = 0.13 + 0.08 \exp(-0.03\tau)$	—	—
CHP	NaBr	1.6	3.0	$c = 0.11 + 0.05 \exp(-0.02\tau)$	—	—
CHP	NBS	0.1	0.1	—	—	—
CHP	thermal decomp.	0.1	0.1	—	—	—
THP	$\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$	130	170	$c = 0.02 + 0.23 \exp(-0.03\tau)$	—	—
THP	$\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ + NaBr	210	270	$c = 0.02 + 0.23 \exp(-0.54\tau)$	—	—
THP	$\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ + NBS	170	55	$c = 0.18 + \exp(-0.57\tau)$	0.57	0.6
THP	NaBr + NBS	5.0	7.6	$c = 0.12 + 0.053 \exp(-0.06\tau)$	0.06	0.01
THP	NaBr	2.5	7.4	$c = 0.1 + 0.063 \exp(-0.02\tau)$	0.02	0.01
THP	NBS	1.25	2.2	$c = 0.1 + 0.06 \exp(-0.01\tau)$	—	—
THP	thermal decomp.	0.13	0.13	—	—	—

in presence of $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ only ($1.2 \cdot 10^{-4}$ mol/l s) and in presence of NaBr solely ($3.00 \cdot 10^{-5}$ mol/l s), is about 2.5 times higher than the sum of both values. The above data allow us to suggest the formation of an active complex between $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ and NaBr.

It should be noted that on the contrary to the observations of other authors⁹, we have observed decomposition of cumene hydroperoxide in presence of NaBr solely. This fact can be interpreted in terms of Denisov concepts¹⁰ illustrated in his study on decomposition of tert-butyl hydroperoxide in presence of $(\text{CH}_3)_4\text{NBr}$ and KBr.

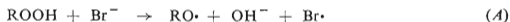
TABLE II
Order with Respect to Cumene Hydroperoxide

Hydroperoxide mol/l	$10^4 \cdot w$, mol/l s		Equation	K , min^{-1}	
	calc.	exp.		calc.	exp.
0.09	1.9	1.4	$c = 0.09 \exp(-0.12\tau)$	0.12	0.09
0.12	1.8	2.2	$c = 0.12 \exp(-0.1\tau)$	0.10	0.09
0.17	3.2	2.8	$c = 0.007 + 0.16 \exp(-0.12\tau)$	0.12	0.10
0.20	3.8	3.1	$c = 0.006 + 0.019 \exp(-0.12\tau)$	0.12	0.10
0.23	3.9	3.4	$c = 0.01 + 0.22 \exp(-0.11\tau)$	0.11	0.10
0.31	6.4	6.1	$c = 0.05 + 0.26 \exp(-0.15\tau)$	0.15	0.10

Order with respect to the catalyst $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O} \cdot 10^{-3}$ and activator (NaBr)

Catal. conc. Activator mol/l	$10^4 \cdot w$, mol/l s		Equation	K , min^{-1}	
	calc.	exp.		calc.	exp.
1.25	0.55	0.71	$c = 0.075 + 0.13 \exp(-0.025\tau)$	0.025	0.011
2.50					
2.50					
5.00	2.3	2.0	$c = 0.05 + 0.16 \exp(-0.09\tau)$	0.09	0.04
10.00					
20.00	7.2	6.6	$c = 0.20 \exp(-0.22\tau)$	0.22	0.22
6.50					
13.00	7.1	5.5	$c = 0.02 + 0.21 \exp(-0.20\tau)$	0.20	0.15
8.50	7.7	5.8	$c = 0.01 + 0.20 \exp(-0.23\tau)$	0.23	0.18
17.00					
5.00					
10.00	3.6	3.2	$c = 0.19 \exp(-0.11\tau)$	0.11	0.11

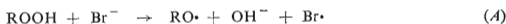
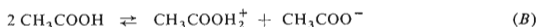
He assumed an interaction occurring between the hydroperoxide and the bromine anion with transfer of an electron.



The decomposition in presence of NaBr proceeds according to a complex relationship which after the processing of the experimental results with a computer may be described by the following expression:

$$c(\text{ROOH}) = 0.11 + 0.054 \exp(-0.02\tau), \quad (I)$$

where τ is time in min. It is seen from this expression that the decomposition proceeds neither according to a first order nor according to a second order reaction with respect to the hydroperoxide. In agreement with the existing concepts the decomposition of hydroperoxides in presence of bromides only, may be described by the following equations:

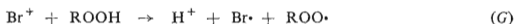
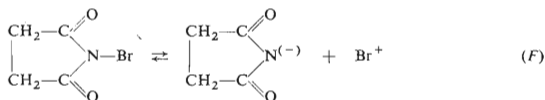


Since the first three reactions proceed at a very high rate, it can be assumed that reaction (A) is the rate determining step. This reaction shows a simple first order relationship with respect to the hydroperoxide. The results obtained by us on decomposition of cumene hydroperoxide reveal a more complex relation. The latter may be explained with the possibility of a preliminary association between Br^- and ROOH resulting from the hydrogen bonding formation.

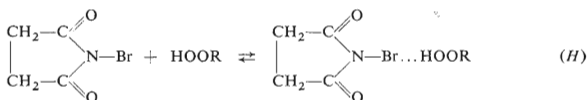


The presence of NBS, an activator of the oxidation of methylaromatic hydrocarbons, does not accelerate the decomposition of cumene hydroperoxide whereas it has an accelerating effect on the decomposition of tetralin hydroperoxide.

The mechanism of decomposition of tetralin hydroperoxide in presence of NBS may be described by the equations given below. As is known¹⁹ NBS undergoes heterolytic decomposition in polar solvents.



The decomposition of tetralin and cumene hydroperoxides in presence of NaBr is not first order with respect to THP (Table I), which shows that in this case the reaction proceeds also according to a more complex mechanism *via* an intermediate complex formation.



With the aim of checking the above assumption the IR spectra of cumene hydroperoxide, NBS and of tetralin hydroperoxide and NBS were taken. In Fig. 5 are shown the spectra of CHP, NBS and of both CHP and NBS, while in Fig. 6 are given the spectra of THP and of both THP and NBS. It is seen that in both cases with hydroperoxide and NBS, a peak is observed at 3420 cm^{-1} due to the formation of hydrogen bonding. No alteration of the peak in the $1600\text{--}1800\text{ cm}^{-1}$ region

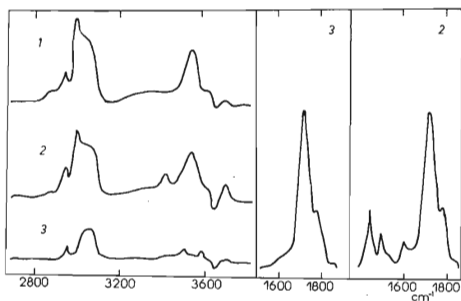


FIG. 5
IR Spectra in Chloroform of 1 CHP, 2 CHP and NBS, 3 NBS

(CO group) is observed, which shows that the hydrogen bond is formed as a result of a bromine ions-hydroperoxide interaction.

The spectra of both hydroperoxides (CHP and THP) were taken in solution in presence of chloroform and acetic acid. The presence of acetic acid does not lead to a peak in the 3420 cm^{-1} region, characterizing the formation of hydrogen bonding between CH_3COOH and the hydroperoxide (Fig. 7).

The different reactions of tetralin and cumene hydroperoxides in presence of NBS may be explained with the possibility of existence of a different type hydroperoxide association²⁰. It is known that the formation of both cyclic and linear associates is possible. Obviously, NBS affects the association of the hydroperoxides, which leads to their different reactivities. Along with the possibility of existence of various types of associates, which affect the rate of decomposition of the hydroperoxides, the difference in the rate of decomposition of CHP and THP in presence of NBS may also be explained with the different rate constants of termination reactions between tetralyl and cumyl peroxy radicals, of the order of 10^3 . In presence of decomposition medium of acetic acid and pseudocumene, a partial regeneration of the initial hydroperoxides is possible^{21,22}. However, this possibility is not supported by our experimental results, since upon decomposition of CHP and THP in presence of NaBr the rates of decomposition are almost equal. If the above-mentioned effect was present, it would follow that in presence of sodium bromide a significant difference in the rates of decomposition of both hydroperoxides can be observed, since the nature of the free radicals obtained is the same.

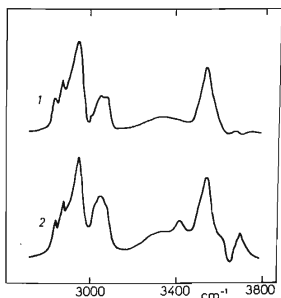


FIG. 6
IR Spectra in Chloroform of 1 THP, 2 THP
and NBS

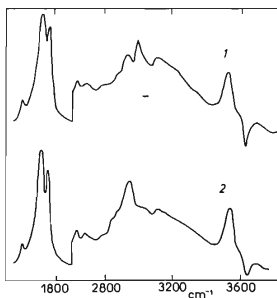


FIG. 7
IR Spectra in Acetic Acid and Chloroform
of 1 CHP, 2 THP

The decomposition of cumene hydroperoxide in presence of $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$, $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ and NaBr and $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ and NBS is a first order reaction with respect to the hydroperoxide. This can be illustrated by the fact that the rate constants calculated by the computers and the experimentally determined ones coincide (Table I). The first order with respect to cumene hydroperoxide obtained on its decomposition in acetic acid–pseudocumene solution agrees with the results achieved in other works^{9,20} in which the decomposition of cumene hydroperoxide in presence of cobalt acetate has been studied.

The obtained data on decomposition of CHP and THP in presence of $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ and NaBr show that no retardation in the rate of decomposition is observed, *i.e.* no induction periods. This shows that in the latter case, similarly to the results obtained in ref.¹², the active form of the catalyst decomposing CHP and THP is also the cobalt monobromide form.

The decomposition of CHP in presence of $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ and NaBr was studied in detail. The dependences of the rate of decomposition on the concentration of the hydroperoxide (Fig. 8) and on the catalyst concentration (Fig. 9) show first order both with respect to the hydroperoxide and the catalyst. The experimentally determined rate constant was compared to that calculated by the computer ($2 \cdot 10^{-3} \text{ s}^{-1}$).

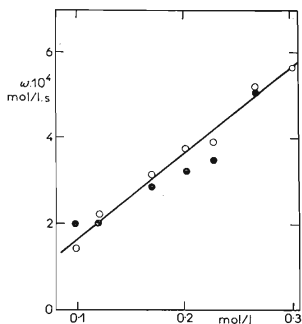


FIG. 8

Dependence of the Initial Rate of Decomposition of Cumene Hydroperoxide on Its Initial Concentration

○ Experimental values, ● calculated values.

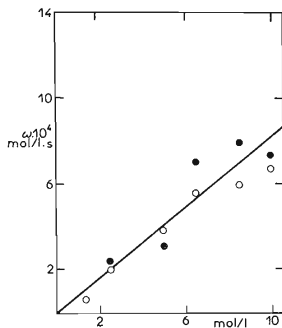


FIG. 9

Dependence of the Initial Rate of Decomposition of Cumene Hydroperoxide on the Concentration of the $\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}$ Catalyst and NaBr Activator

○ Experimental values, ● calculated values.

Thus the following expression was experimentally obtained

$$-dc(\text{ROOH})/dt = k_{\text{ef}}c(\text{ROOH}), \quad (2)$$

where $k_{\text{ef}} = k_1c(\text{CoAc}_2 \cdot 4 \text{H}_2\text{O})$, $k_1 = kc(\text{NaBr})$ or $k_1 = kc(\text{NBS})$. The decomposition of cumene hydroperoxide in the presence of cobalt acetate and bromium activator can be expressed by the following equation

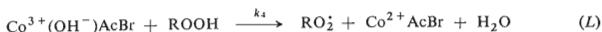
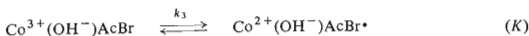
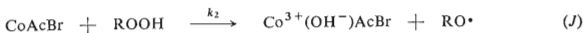
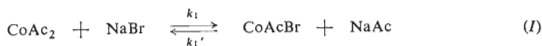
$$w = -dc(\text{ROOH})/dt = kc(\text{NaBr})c(\text{CoAc}_2 \cdot 4 \text{H}_2\text{O}) = 0.4c(\text{ROOH}). \quad (3)$$

In a previous work we have shown that the initiation rate on interaction between CoAcBr complex and ROOH is significantly lower than the experimentally measured one¹. The value of the rate constant of decomposition k_{ef} obtained in an earlier work was 0.23 mol/l s while the corrected value of this constant given in the present work is 0.4 mol/l s which shows the results obtained coincide satisfactorily.

The value of the initiation rate measured experimentally is $3.4 \cdot 10^{-6}$ l/mol s, whereas in case of the corrected value of the rate constant (0.4 l/mol s the rate of initiation is of the order of $1 \cdot 10^{-10}$ l/mol s. This indicates the presence of a direct initiation *via* an intermediate complex formation between CoAcBr complex, oxygen and the hydrocarbon.

The rate of decomposition of CHP in presence of both CoAc₂·4 H₂O and NaBr, as already mentioned, is considerably higher than that of a decomposition proceeding in presence of CoAc₂·4 H₂O only or with NaBr solely which shows that the main part of the hydroperoxide decomposes not under the action of CoAc₂·4 H₂O but by the more active cobalt acetate bromide complex. During the decomposition Co²⁺ is converted into Co³⁺. This can be confirmed by the change of colour in the course of the reaction and also by the fact that the catalytic CoAcBr complex decomposes by two orders higher amount of hydroperoxide as compared to the concentration of the catalyst.

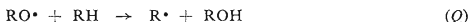
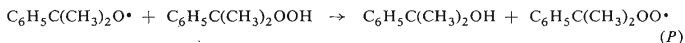
The decomposition of the hydroperoxide in presence of the cobalt acetate bromide complex may be expressed by the following schemes:



The suggested mechanism of decomposition of cumene hydroperoxide in presence of CoAcBr is supported by the results from the analyses with gas-liquid chromatography. In Fig. 10 is shown the chromatograph obtained on analysis of the products of decomposition of cumene hydroperoxide in the presence of CoAc₂·4 H₂O and of both CoAc₂·4 H₂O and NaBr. The amount of dimethylphenylcarbinol is considerably higher than that of acetophenone. The destroying of the free valence does not proceed in acetophenone and dimethylphenylcarbinol by recombination of the peroxide radicals since they should be obtained in equal amounts²³. Acetophenone is obtained as a result of a radical conversion.



Dimethylphenylcarbinol is formed as a result of the interaction of an alkyl oxide radical and the hydroperoxide or the hydrocarbon.



The processing of the proposed scheme of catalytic decomposition of cumene hydroperoxide under action of CoAcBr leads to the following expression

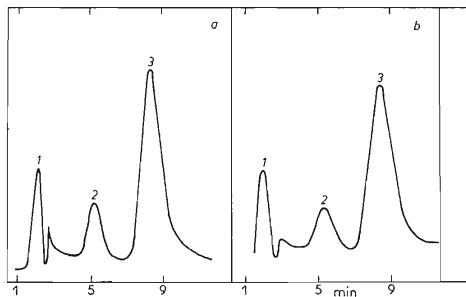


FIG. 10

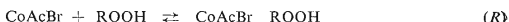
Chromatogram of the Products of Decomposition of Cumene Hydroperoxide

a) In the presence of CoAc₂·4 H₂O and NaBr: 1 pseudocumene, 2 acetophenone, 3 dimethylphenylcarbinol. b) In the presence of CoAc₂·4 H₂O: 1 pseudocumene, 2 acetophenone, 3 dimethylphenylcarbinol.

$$w = -dc(\text{ROOH})/dt = 2k_2Kc(\text{CoAc}_2)c(\text{NaBr})c(\text{ROOH}) = k_1c(\text{CoAc}_2)c(\text{ROOH}) = k_{\text{eff}}c(\text{ROOH}) \quad (4)$$

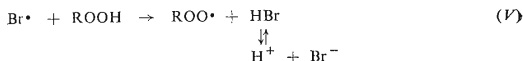
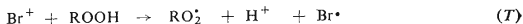
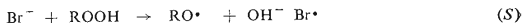
where $k_1 = 2k_2Kc(\text{NaBr})$. The obtained expression is analogous to the empiric one.

It is known²⁴⁻³² that the experimental data obtained on catalytic decomposition of the hydroperoxides only in presence of catalysts satisfy the Michaelis-Menten equation. The reaction proceeds according to the above scheme provided a preliminary complex formation between the catalyst and the substrate (hydroperoxide) is present. Cobalt acetate is modified into CoAcBr , which shifts the equilibrium of the reaction to the left.



During decomposition of tetralin hydroperoxide highest rates are also observed in presence of both $\text{CoAc}_2 \cdot 4\text{H}_2\text{O}$ and NaBr (Table I). The reaction is of first order when the decomposition occurs only in the presence of $\text{CoAc}_2 \cdot 4\text{H}_2\text{O}$ as well as in the presence of both $\text{CoAc}_2 \cdot 4\text{H}_2\text{O}$ and NaBr . It can be assumed that the mechanism of decomposition of tetralin hydroperoxide is analogous to that of cumene hydroperoxide. When NBS is used as activator the reaction does not follow a first order relation which shows that a more detailed study of the decomposition of THP in presence of this system is necessary in order to establish the order and mechanism of the reaction.

The data from Table I demonstrate the decomposition of tetralin hydroperoxide in the presence of NaBr only and in the presence of NBS. The rate of decomposition in the presence of NaBr is about two times higher than that with NBS. In the case of cumene hydroperoxide, decomposition in the presence of NBS is not observed. This gives us grounds to suggest that bromium anions obtained in the system will facilitate the decomposition of the peroxides as the electron $\text{Br}^- \rightarrow \text{O}$ transfer is probably favoured compared to the $\text{H} \rightarrow \text{Br}^+$ transfer. The use of a NBS— NaBr mixture increases significantly the rate of decomposition of both tetralin and cumene hydroperoxides. The synergetic effect may be explained with the following reactions:



The additional amount of HBr leads to an increase of the concentration of the more active peroxide decomposing agent Br^- .

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